

NOVEL INORGANIC RING SYSTEMS

XXXIX *. A DIMERIC CYCLOALUMADISILATRIAZANE **

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Summary

The first cycloalumadisilatriazane system, $[\text{ClAl}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ (**C1**), has been prepared. IR and Raman spectra are reported. The molar weight of **C1** in benzene and ^1H , ^{13}C , ^{27}Al and ^{29}Si NMR spectra are consistent with a nitrogen-bridged dimer which is stereochemically rigid on the NMR time scale near room temperature. Mass spectral evidence is also presented for the dimeric nature of **C1** in the gas phase. **C1** crystallizes in the triclinic space group $P\bar{1}$ with a 8.2262(7) Å, b 9.5147(7) Å, c 10.2552(6) Å, α 102.655(5)°, β 97.448(5)°, γ 112.088(6)° and $Z = 1$. The structure was refined to an R value of 0.0303 for 2487 counter-measured, observed X-ray data. The mean Al–N bridging distance (1.947(8) Å) in the centrosymmetric (Al–N) $_2$ ring is much longer than the Al–N(cn3) bond (cn = coordination number), 1.803(2) Å. A smaller dependence on nitrogen valency was found for the Si–N bond lengths; thus the Si–N(cn 4) and mean Si–N(cn 3) are 1.798(2) and 1.726(14) Å, respectively.

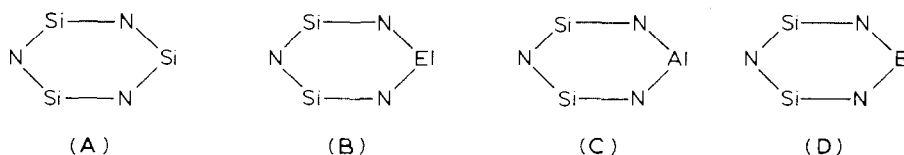
Introduction

The Si_3N_3 framework **A** of cyclotrisilazane was the first observed silicon–nitrogen ring system [3]. We later generated the six-membered symmetric “hetero”cyclosilazanes **B** by replacing one of the silicon atoms of **A** by almost all of the important main group elements, e.g. El = Be, B, C, Ge, Sn, P, As, Sb, S [4]. Our interest has

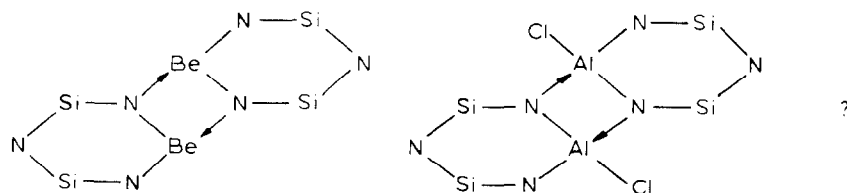
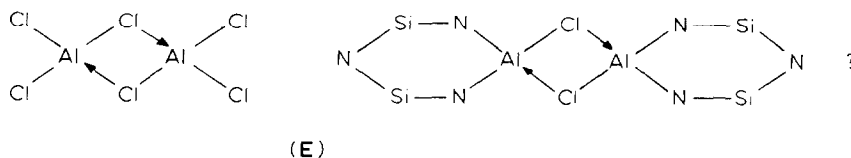
* For part XXXVIII see ref. 1. Also: Contributions to the chemistry of SiN compounds. CLX. For part CLIX see ref. 2.

** Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983.

now been directed towards the synthesis of a hitherto unknown "hetero" cyclosilazane **C**.

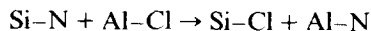


The extent of association of **C** was a feature of considerable interest since the boron analogue **D** is monomeric while many Al-N compounds form dimers or higher oligomers. Furthermore, since AlCl_3 was used as a starting material, association might occur as in AlCl_3 itself via chlorine bridges (case **E**) or, by analogy to the beryllium system [5], via Al-N coordination (case **F**).

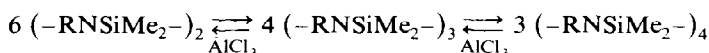


Preparation of dimeric 1-chloro-2,3,3,4,5,5,6-heptamethylcyclo-1-aluma-3,5-disila-2,4,6-triazane (**C1**)

Attempts to prepare **C** were made by reactions 1 and 2; i.e., lithiation of bis(methylamino)pentamethyldisilazane (**I**) and subsequent reaction with aluminium trichloride in the presence of triethylamine. Important side reactions here might be the known cleavage of Si-N bonds by AlCl bonds accompanied by substituent exchange [6]:



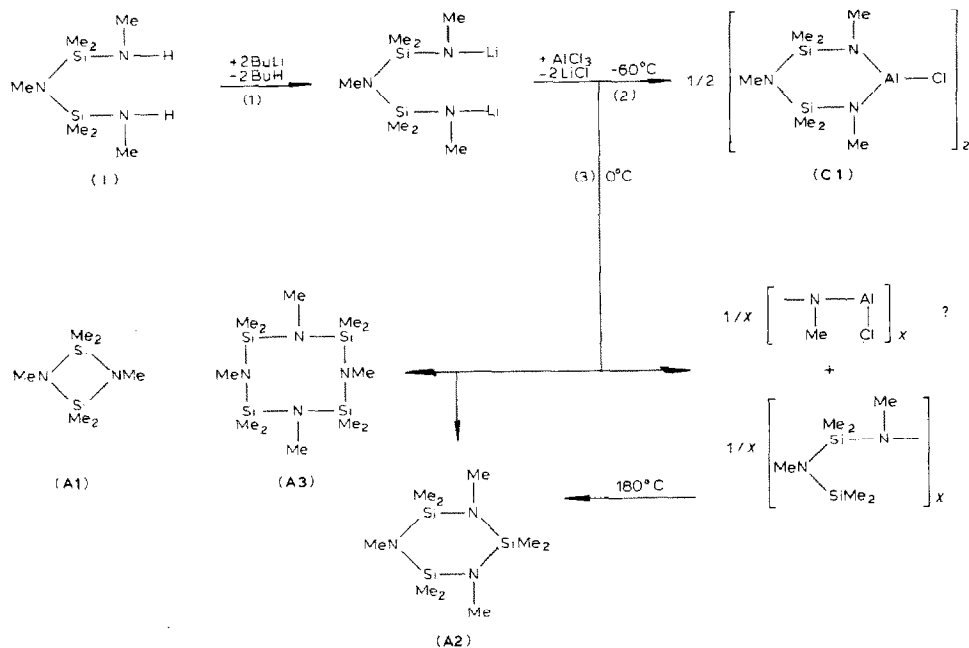
In the presence of AlCl_3 cyclosilazanes may also undergo ring contractions and ring expansions, with the six-membered ring as the main component in this system [7]:



Such side reactions may be responsible for the fact that the reaction of AlCl_3 with $\text{MeN}(\text{SiMe}_2\text{NMeLi})_2$ in benzene/triethylamine solution at 0°C (reactions 1 and 3) yields only red-brown polymeric material and a liquid phase, which contained, according to mass spectral analysis*, some hexamethylcyclodisilazane (**A1**), nonamethylcyclotrisilazane (**A2**), dodecamethylcyclotetrasilazane (**A3**), and a high boiling

* Among others $m/e = 348$ (1) M^+ of **A3**, 333(6) $[M-\text{CH}_3]^+$ of **A3**, 261(18) M^+ of **A2**, 246(100) $[M-\text{CH}_3]^+$ of **A2**, 159(38) $[M-\text{CH}_3]^+$ of **A1**(?).

product which decomposed at 180°C and 0.001 torr to give more **A2** **. But at -60°C the reaction with AlCl₃ followed route 2, the cycloalumasilizane **C1** being isolated in yields of > 20%.



The large, block-shaped, colourless crystals of **C1** which melt at 170°C (dec.) are soluble in petroleum ether but less so in carbon tetrachloride and benzene. They are very sensitive to moisture and decompose rapidly on contact with air, first becoming opaque and later being transformed into a white amorphous mass.

Proof of composition and structure

Elemental analysis: Found: C, 31.62; H, 7.96; Al, 10.15; Cl, 13.33; N, 15.80; Si, 21.13. Mol. weight 595 g mol⁻¹ (cryosc. in benzene) C₁₄H₄₂Al₂Cl₂N₆Si₄. Calcd.: mol. weight 531.74 g mol⁻¹ C, 31.9; H, 8.3; Cl, 13.6; N, 15.9; Si, 21.2%; Al: strong positive reaction with aurintricarboxylic acid.

NMR spectra

C1 was studied by ¹H, ¹³C, ²⁷Al and ²⁹Si NMR spectroscopy. The data are given in Table 1 and Fig. 1 and are wholly consistent with a rigid molecule which is an oligomer of an AlSi₂N₃ heterocycle. All the evidence favours the presence of a dimer in solution, though a trimer or other oligomers cannot be fully excluded on the basis of NMR spectra alone.

The ¹H NMR spectrum exhibits 3 sharp singlets in the NCH₃ region and 4 sharp singlets in the SiCH₃ region. The relative intensities are in full agreement with a composition AlClSi(CH₃)₄N(CH₃)₃. Table 1 and Fig. 1 reveal the large solvent

** B.p. 32°C/0.001 Torr, m.p. 35°C, ¹H NMR: τ = 9.78 (s, 18H, SiCH₃), 7.55 (s, 9H, NCH₃); m/e = 261(17) M⁺, 246(100) [M - CH₃]⁺.

TABLE I
NMR SPECTRA OF C1

Nucleus	Solvent	Standard	Chemical shift ^a				
¹ H	C ₆ H ₆	int. TMS	0.14	0.17	0.20	0.27	SiCH ₃
			2.46	2.53	2.64		NCH ₃
	C ₆ D ₆	int. C ₆ HD ₅	0.276	0.295	0.313	0.383	SiCH ₃
			2.534	2.651	2.767		NCH ₃
	CDCl ₃	int. CHCl ₃	0.065	0.113	0.279	0.369	SiCH ₃
2.541			2.553	2.560		NCH ₃	
¹³ C	C ₆ H ₆ /C ₆ D ₆	int. TMS	-3.1	-1.2	-0.2	+1.3	SiC
			29.9	31.1	32.4		NC
²⁹ Si	C ₆ D ₆	int. TMS	4.0	11.6			
²⁷ Al	CDCl ₃	ext. Al(OH ₂) ₆ ³⁺	112				

^a Chemical shift δ in ppm; high frequency = positive sign.

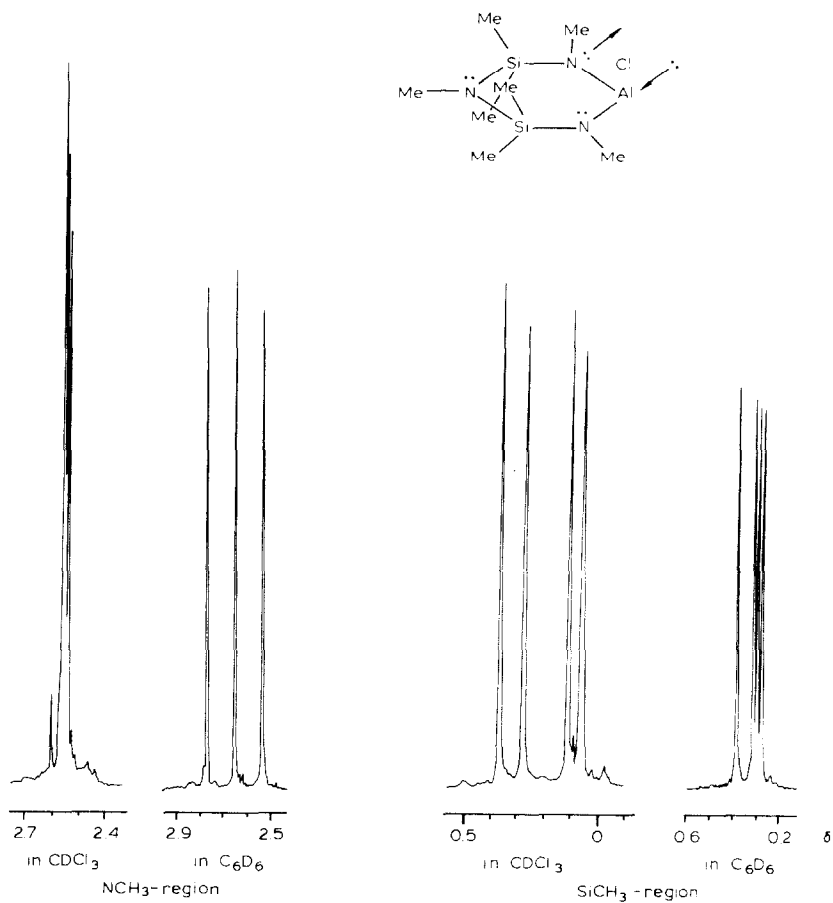


Fig. 1. ¹H NMR spectra of C1.

dependence of the proton chemical shifts. The occurrence of seven different signals from the methyl groups suggests the conformation shown in Fig. 1.

The ^{13}C spectrum shows exactly the same pattern, with 3 singlets due to C(N) and 4 singlets due to C(Si) nuclei. All the signals have the same intensity, and the NCH_3 and SiCH_3 resonances fall into narrow but diagnostic ranges.

The two sharp singlets observed in the ^{29}Si spectrum confirm the presence of two different Si atoms. The ^{29}Si chemical shifts of nitrogen-linked methylsilicon groups are close to TMS [8,9]. By comparison with the data for $(\text{Me}_3\text{Si})_2\text{NMe}$ and $(\text{Me}_2\text{SiNH})_3$, the low and high frequency signals are tentatively assigned to the $\text{N}(\text{cn}3)\text{SiN}(\text{cn}3)$ and the $\text{N}(\text{cn}4)\text{SiN}(\text{cn}3)$ atoms (cn = coordination number), respectively. The ^{27}Al resonance is found within the wide range observed for tetracoordinated Al [10].

Vibrational spectra

C1 has been investigated by IR and Raman spectroscopy. The observed vibrational frequencies are listed in Table 2.

Though no complete assignment will be attempted here, some characteristic frequencies of the increments follow from comparison with spectra of some simple metal derivatives of the heptamethyldisilatriazane ligand [11,12]. Several of the NCH_3 vibrations are split, and similar multiplicity is observed for the SiC stretching vibrations; this is consistent with the low symmetry of the molecular fragments.

The strong IR absorption near 600 cm^{-1} is clearly associated with an AlCl stretching vibration; cf. 606 and 625 cm^{-1} for the terminal asymmetric AlCl

TABLE 2
IR AND RAMAN SPECTRA OF **C1** (cm^{-1})

IR	Raman	Assignment	IR	Raman	Assignment
	117 m	deformations	733 vs	768 w 788 m	$\nu_{\text{as}}(\text{SiC}_2)$
	148 m		764 m		
	180 m		789 vs		
	221 s		795 sh		
290 m	321 m	skeletal vibrations	827 m	890 vw 910 vw 971 m	$\nu_{\text{as}}(\text{SiNSi})$ (ring)
320 w			364 vs		
373 s	384 w		896 vs		
			906 vs		
396 m	420 vs		1004 vw	1001 w	$\nu(\text{CN})$
462 s			1056 vs		
	508 s	$\nu(\text{AlCl})$	1080 s	1085 vw	$\rho(\text{NCH}_3)$
	523 w		1154 w		
543 vs	556 s		1169 s		
560 s			1258 vs		
597 vs			1255 w	1412 m 1435 m 1462 m	$\delta_{\text{as}}(\text{SiCH}_3)$ $\delta_{\text{as}}(\text{CH}_3)$
650 w					
670 vw	671 w				
686 vw	687 s	$\nu_{\text{s}}(\text{SiC}_2)$			
692 vw					

TABLE 3
SELECTED MASS SPECTRAL DATA FOR C1

Ionization potential	(eV)	70	40	40	40
Inlet temperature	(°C)	100	150	175	200
<i>m/e</i>	fragment	relative intensities			
530/532	M^+	27.6	18.9	16.0	12.7
515/517	$[M - \text{CH}_3]^+$	100	100	100	100
266/268	$[M/2 + \text{H}]^+$	63.8	45.3	68.0	49.0
250/252	$[M/2 - \text{CH}_3]^+$	58.6	11.8	19.0	19.6

M^+ $\text{C}_{14}\text{H}_{42}\text{Al}_2\text{Cl}_2\text{N}_6\text{Si}_4$			$[M/2 + \text{H}]^+$ $\text{C}_7\text{H}_{22}\text{AlClN}_3\text{Si}_2$		
<i>m/e</i>	intensity		<i>m/e</i>	intensity	
	calcd.	found		calcd.	found
530	100	100	266	100	100
531	38.9	37	267	19.5	14
532	84.3	83	268	40.3	39
533	30.2	29	269	7.2	7
534	24.7	24	270	2.8	3

stretches in Al_2Cl_6 [13]. The two strongest Raman lines located at 420 and 364 cm^{-1} probably involve the breathing of the six- and four-membered rings.

Mass spectra

In contrast to the very confusing mass spectrum of the Be compound **F**, the mass spectrum of **C1** is very simple and shows only a few fragments. Even at various ionization potentials and inlet temperatures, the dimeric form of **C1** gives the strongest peak. There are only two signals in this region, M^+ and $[M - \text{CH}_3]^+$, the latter being the base peak (Table 3). The remaining peaks fall in the range of monomeric **C1**, the two main peaks being $[M/2 + \text{H}]^+$ and $[M/2 - \text{CH}_3]^+$. The relation between the fragments of the dimeric and the monomeric form is nearly independent of temperature and ionization potential. Peak 266 is not a signal caused by M^{2+} , as can be seen from the calculated and observed intensity of the isotope pattern (Table 3).

In addition to the ions mentioned above, others are observed which are not derived from **C1** but from products of decomposition by routes similar to reaction 3. Peaks at $m/e = 261$ (M^+ of **A2**) and (even higher in intensity) at $m/e = 246$ ($[M - \text{CH}_3]^+$ of **A2**) are observed in all cases, and we also found ions at $m/e = 333$ ($[M - \text{CH}_3]^+$ of **A3**) and 159 ($[M - \text{CH}_3]^+$ of **A1**). **A1**–**A3** are not impurities in **C1**; they are formed during the short period of heating for inlet temperature. If **C1** is kept at 100–150°C for 30 h, no **C1** fragments are detected at all in the mass spectrum but only large amounts of **A1**–**A3** fragment signals. It is clear that the ion of $m/e = 266$ ($[M/2 + \text{H}]^+$) is not formed by primary thermal decomposition of M ($\rightarrow 2M/2$) but from decomposition of M^+ or $[M - \text{CH}_3]^+$ in the mass spectrometer.

TABLE 4
CRYSTAL DATA FOR C1

Formula	$\{ClAl[N(CH_3)Si(CH_3)_2]_2NCH_3\}_2$
Crystal system	triclinic
<i>a</i>	8.2262(7) Å
<i>b</i>	9.5147(7) Å
<i>c</i>	10.2552(6) Å
α	102.655(5)°
β	97.448(5)°
γ	112.088(6)°
<i>Z</i>	1
<i>d_c</i>	1.252 g/cm ³
<i>t</i>	20°C
Space group	$P\bar{1}$
Quadrants measured	$hkl, \bar{h}kl, h\bar{k}l, \bar{h}\bar{k}l$
λ	0.71069 Å
Monochromator	graphite
Maximum θ	27.44°
Scan technique	$\omega-2\theta$
Scan width (ω)	0.70° + 0.34° tan θ
Scan speed (2 θ)	0.55–5.00°/min
Reflections measured	3177
Observed ($ F_0 \geq 4\sigma(F_0)$)	2487
Weights <i>w</i> observed	$[\sigma^2(F_0) + 0.0004 F_0 ^2]^{-1}$
Unobserved	0
μ (Mo- K_α)	4.7 cm ⁻¹

X-ray structure analysis

A crystal of C1 was sealed in a glass capillary under argon. Diffraction measurements were made with a CAD-4 diffractometer. A search of reciprocal space yielded a triclinic unit cell, which was shown to be the cell of highest symmetry by a reduced cell calculation. ω scans of three strong, low angle reflections and fast $\omega-2\theta$ scans of 1717 peaks confirmed the suitability of the crystal for an X-ray study.

Intensity measurements were made with the previously described [14] $\omega-2\theta$ scan technique. During data collection, the intensities of three periodically-monitored standard reflections showed no significant drift. The data were reduced to $|F_0|$'s, an absorption correction being deemed unnecessary. Crystal data and pertinent experimental details appear in Table 4.

All calculations were made in the space group $P\bar{1}$, the successful refinement of the structure confirming this choice. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The function minimized was $\Sigma w\Delta^2$, $\Delta = ||F_0| - |F_c||$. Dispersion corrected [15], relativistic Hartree-Fock scattering factors were used for all atoms except H, for which SDS values were applied [16]. Hydrogen coordinates were taken from a difference Fourier map and idealised (C–H = 0.95 Å, H–C–H = 109.47°). The resulting CH₃ fragments were varied as rigid groups with a common isotropic thermal parameter for the H atoms. Refinement converged, maximum $|\zeta/\sigma| = 0.1$, with $R = \Sigma\Delta/\Sigma|F_0| = 0.0303$ for all observed reflections, $R = 0.0457$ for all reflections and $R_w = [\Sigma w\Delta^2/\Sigma w|F_0|^2]^{1/2} = 0.0424$. A difference Fourier synthesis contained densities between 0.5 and -0.3 e/Å³, thus confirming

(Continued on p. 42)

TABLE 5

POSITIONAL AND THERMAL h^2c PARAMETERS FOR THE NONHYDROGEN ATOMS OF Cl

Atom	x	y	z	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Cl	24546(7)	61182(7)	30462(5)	568(3)	633(3)	496(3)	95(3)	313(3)	108(2)
Si(1)	26250(7)	60124(6)	75397(5)	358(3)	368(3)	374(3)	143(2)	81(2)	87(2)
Si(2)	21324(7)	90060(6)	74773(5)	434(3)	299(2)	421(3)	121(2)	87(2)	30(2)
Al	11882(7)	63028(6)	47333(5)	326(3)	304(3)	344(3)	72(2)	125(2)	72(2)
N(1)	1428(2)	4902(2)	5791(1)	320(7)	310(7)	381(8)	130(6)	113(6)	52(6)
N(2)	1753(2)	7361(2)	8080(2)	428(8)	370(8)	370(8)	150(7)	173(6)	85(6)
N(3)	1984(2)	8338(2)	5750(2)	425(9)	297(7)	413(8)	89(6)	86(7)	111(6)
C(1)	2323(3)	3848(2)	5196(2)	47(1)	44(1)	65(1)	23(1)	18(1)	2(1)
C(2)	5058(3)	7008(3)	7534(2)	36(1)	64(1)	62(1)	18(1)	5(1)	-2(1)
C(3)	2381(4)	4647(3)	8620(3)	93(2)	64(2)	61(2)	39(2)	14(1)	28(1)
C(4)	945(3)	7328(3)	9293(2)	66(2)	63(1)	46(1)	24(1)	31(1)	11(1)
C(5)	4391(3)	10672(3)	8345(2)	67(2)	43(1)	53(1)	-2(1)	-1(1)	6(1)
C(6)	429(4)	9800(3)	7876(3)	80(2)	59(2)	70(2)	43(1)	16(1)	2(1)
C(7)	2498(4)	9593(3)	5052(3)	86(2)	43(1)	59(1)	16(1)	13(1)	23(1)

$a \times 10^4$ for N and C atoms, otherwise $\times 10^5$, $b \times 10^3$ for C atoms, otherwise $\times 10^4$. The form of the anisotropic thermal ellipsoids is $\exp[-2\pi^2(U_{1,1}h^2a^{*2} + U_{2,2}k^2b^{*2} + U_{3,3}l^2c^{*2} + 2U_{1,2}hka^*b^* + 2U_{1,3}hla^*c^* + 2U_{2,3}klb^*c^*)]$.

TABLE 6
POSITIONAL ($\times 10^4$)^a AND THERMAL ^b PARAMETERS FOR THE HYDROGEN ATOMS OF Cl

Atom	x	y	z	Atom	x	y	z
H(1A)	1732	3362	4251	H(4C)	992	6480	9620
H(1B)	2200	3053	5645	H(5A)	4584	10939	9318
H(1C)	3567	4467	5281	H(5B)	4480	11575	8055
H(2A)	5713	7799	8384	H(5C)	5277	10336	8070
H(2B)	5191	7478	6804	H(6A)	560	10545	7369
H(2C)	5513	6218	7405	H(6B)	769	10338	8832
H(3A)	2935	3985	8253	H(6C)	-794	9047	7638
H(3B)	1151	4013	8568	H(7A)	2463	9134	4121
H(3C)	2988	5213	9552	H(7B)	3698	10330	5513
H(4A)	1617	8303	9994	H(7C)	1726	10126	5082
H(4B)	-274	7180	9047				

^a The derived standard deviations of the hydrogen fractional coordinates are equal to those of the corresponding carbon atom. ^b The isotropic temperature factors have the form $\exp[-8\pi^2 U \sin^2 \theta / \lambda^2]$ and are 0.095(6), 0.095(6), 0.106(6), 0.118(7), 0.132(8), 0.106(6) and 0.117(7) for H atoms bonded to C(1), C(2), ... C(7), respectively.

TABLE 7
SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN Cl

Al-Cl	2.1404(8)	Si(1)-C(2)	1.867(2)
Al-N(1)	1.941(2)	Si(1)-C(3)	1.857(2)
Al-N(1) ^a	1.952(2)	Si(2)-C(5)	1.870(2)
Al-N(3)	1.803(2)	Si(2)-C(6)	1.874(2)
Si(1)-N(1)	1.798(2)	N(1)-C(1)	1.524(2)
Si(1)-N(2)	1.718(2)	N(2)-C(4)	1.485(2)
Si(2)-N(2)	1.742(2)	N(3)-C(7)	1.481(3)
Si(2)-N(3)	1.717(2)		
Cl-Al-N(1)	110.68(6)	N(3)-Si(2)-C(5)	110.3(1)
Cl-Al-N(1)'	113.55(5)	N(3)-Si(2)-C(6)	113.8(1)
Cl-Al-N(3)	111.23(6)	C(5)-Si(2)-C(6)	105.9(1)
N(1)-Al-N(1)'	90.6(1)	Al-N(1)-Al'	89.4(1)
N(1)-Al-N(3)	113.77(7)	Si(1)-N(1)-Al	110.72(8)
N(1)'-Al-N(3)	115.48(8)	Si(1)-N(1)-Al'	122.22(9)
N(1)-Si(1)-N(2)	107.26(8)	Si(1)-N(1)-C(1)	109.3(1)
N(1)-Si(1)-C(2)	107.0(1)	C(1)-N(1)-Al	114.7(1)
N(1)-Si(1)-C(3)	109.9(1)	C(1)-N(1)-Al'	109.5(1)
N(2)-Si(1)-C(2)	111.8(1)	Si(1)-N(2)-Si(2)	122.7(1)
N(2)-Si(1)-C(3)	112.1(1)	Si(1)-N(2)-C(4)	119.5(2)
C(2)-Si(1)-C(3)	108.7(1)	Si(2)-N(2)-C(4)	116.8(2)
N(2)-Si(2)-N(3)	105.33(8)	Si(2)-N(3)-Al	126.67(9)
N(2)-Si(2)-C(5)	112.6(1)	Si(2)-N(3)-C(7)	118.5(1)
N(2)-Si(2)-C(6)	109.0(1)	Al-N(3)-C(7)	114.7(1)

^a Primed atoms are related to those in the asymmetric unit by $x', y', z' = -x, 1-y, 1-z$.

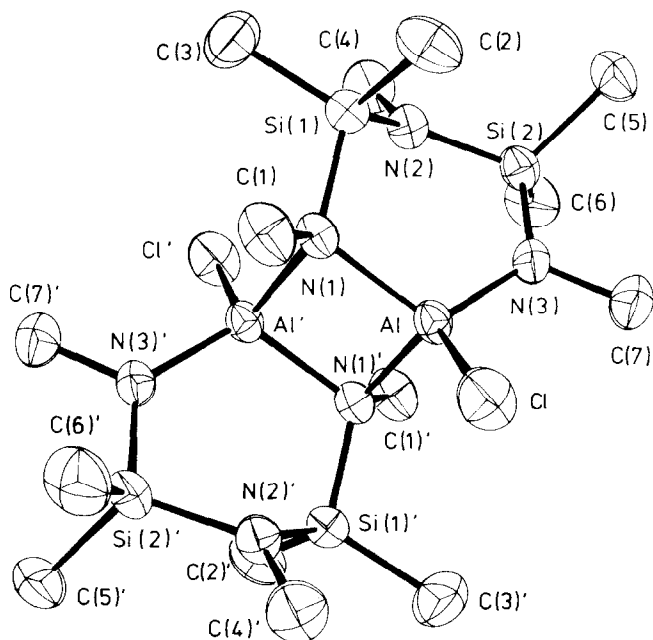


Fig. 2. Perspective drawing of **C1** with 50% probability thermal ellipsoids and hydrogen atoms omitted.

the structure *. Final parameters are listed in Tables 5 and 6. The numbering scheme is defined in Fig. 2, H atoms being given the numbers of the C atoms to which they are attached. Selected bond distances and angles are given in Table 7. Computer programs were described previously [14].

Description of the structure

Crystals of **C1** contain discrete dimeric molecules separated by normal Van der Waals distances, the shortest being H(1C)–H(1C) ($1-x, 1-y, 1-z$), 2.395(4) Å. The tricyclic molecules possess crystallographic $\bar{1}$ symmetry, which requires that the [Al–N(1)]₂ ring be planar. As found in the heterocyclic six-membered rings of (C₆H₅CH₂)₂Ti[N(SiMe₂NMe)₂SiMe₂]₂ (II) [14] and [Be(NMeSiMe₂)₂CH₂]₂ (III) [17], the six-membered rings in **C1** are nonplanar (root-mean-square deviations of 0.26 Å). Its conformation is irregular, best defined by the torsion angles given in Table 8, and different from those in II [14] and III [17]; the latter feature is not surprising, since some of the atoms in the three compounds have different coordination numbers.

Each Al atom binds to one tertiary and two quaternary N atoms. The small but significant, 0.011(2) Å, difference in the Al–N(1) and Al–N(1)' bond lengths may reflect the different conformations of these bonds. For example, along Al–N(1) the

* $|F_0|$, F_c Tables are available from D.J.B. upon request.

TABLE 8
ENDOCYCLIC TORSION ANGLES (°) OF THE SIX-MEMBERED RING IN Cl

Al–N(1)–Si(1)–N(2)	44.8	N(2)–Si(2)–N(3)–Al	10.5
N(1)–Si(1)–N(2)–Si(2)	–71.0	Si(2)–N(3)–Al–N(1)	–25.0
Si(1)–N(2)–Si(2)–N(3)	40.4	N(3)–Al–N(1)–Si(1)	–6.1

N(1)–Si(1) and Al–N(3) bonds are approximately eclipsed while along Al–N(1)' the N(1)'–Si(1)' and Al–Cl bonds are eclipsed. The distance to the tertiary N atom is 0.144(8) Å shorter than the average of the other Al–N bond lengths. This dependence on N coordination number agrees with that found in previous studies (Table 9).

The Si(1)–N(1) bond length is 0.072(14) Å longer than the average of the three Si–N(cn 3) bond lengths, and is compared with other Si–N(cn 4) bond distances in Table 9. Perhaps the 8 σ deviation in the Si(1)–N(2) and Si(2)–N(2) bond lengths reflects the different extents to which N(1) and N(3) have satisfied the valencies of Si(1) and Si(2), respectively. An additional indication that N(2)–Si(1) is stronger than N(2)–Si(2) may be the fact that the angle C(4)–N(2)–Si(1) is 2.7(2)° larger than C(4)–N(2)–Si(2); however, caution is required here since the N(2)–C(4) and Si(1)–C(3) bonds are eclipsed.

The degree of N(2) and N(3) planarity may be judged from the respective deviations, 0.098(2) and 0.024(2) Å, of these atoms from the planes through their substituents. Their average N–C bond distance, 1.483(3) Å, is unexceptional but 10 σ, 0.041(4) Å, shorter than N(1)–C(1). The C(7)–N(3)–Al bond angle is 3.8(2)°

TABLE 9
COMPARISON OF SELECTED^a Al–N AND Si–N BOND LENGTHS

Compound	Bond type	M–N (Å)	Ref.
Al[N(SiMe ₃) ₂] ₃	(cn3)Al–N(cn3)	1.78(2)	23
Cl ₂ AlNEtC ₂ H ₄ NMe ₂	(cn4)Al–N(cn3)	1.770(2)	24
Al ₄ Cl ₄ (NMe ₂) ₄ (NMe) ₂		1.79(3)	25
[ClAl(NMeSiMe ₂) ₂ NMe] ₂		1.803(2)	this study
Me ₂ Si(N ^t Bu) ₂ AlPh·AlPh ₃ ^b		1.98	22
Al–N-Clusters	(cn4)Al–N(cn4)	1.916(6)	^c
Cl ₂ AlNMe ₂		1.910(4)	26
		1.961(6)	27
[ClAl(NMeSiMe ₂) ₂ NMe] ₂		1.947(8)	this study
(Me ₂ AlNMe ₂) ₂		1.961(11)	28,29
Me ₂ Si(N ^t Bu) ₂ AlPh·AlPh ₃ ^b		2.00	22
[NaN(SiMe ₃) ₂] _∞	(cn4)Si–N(cn4)	1.690(5)	20
[LiN(SiMe ₃) ₂] ₃		1.729(4)	30
[Be(NMeSiMe ₂) ₂ CH ₂] ₂		1.752(2)	17
(CO) ₁₀ Fe ₃ NSiMe ₃		1.779(10)	31
[ClAl(NMeSiMe ₂) ₂ NMe] ₂		1.798(2)	this study
Me ₂ Si(N ^t Bu) ₂ AlPh·AlPh ₃ ^b		1.82	22

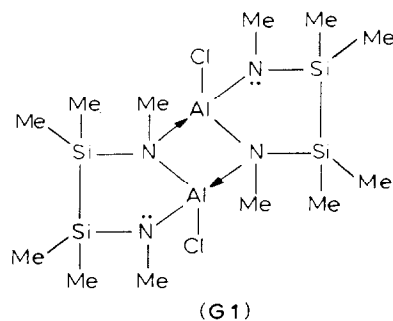
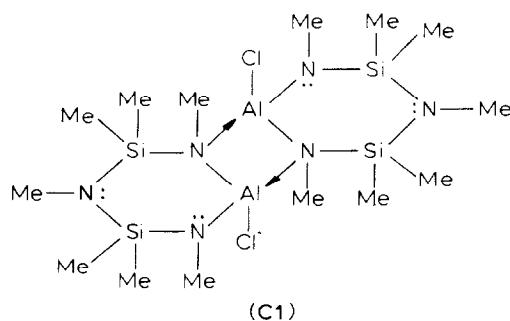
^a Data on compounds with multiple C,N bonds were omitted. ^b Al takes part in 3z2e bonds ^c Average of mean values found in eight aluminum imide clusters under ref. 32–37.

larger than C(7)–N(3)–Si(2), perhaps because the Al–N(3) linkage is more ionic than that of Si(2)–N(3) or because the cross-angle repulsion radius of an Al atom exceeds that of an Si atom [18]. The Al–Cl and Si–C valencies are normal.

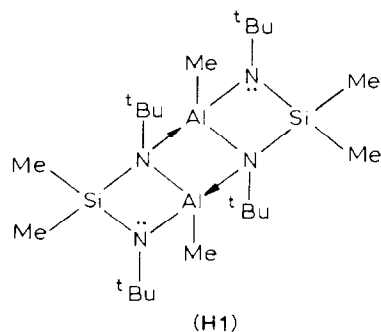
Discussion

In non-polar solvents at room temperature, **C1** is rigid on the NMR time scale. The NMR studies exclude the presence of a monomer $\text{ClAl}(\text{NMeSiMe}_2)_2\text{NMe}$, and there is no indication of an equilibrium between oligomers at 300 K, as was observed for $\text{LiN}(\text{SiMe}_3)_2$ [19]. The possibility of dynamic behaviour at higher temperature was not investigated. Such dynamic behaviour resulting in equivalence of Be(cn3) and N(cn4) was deduced from the ^1H NMR spectra of $[\text{Be}(\text{NMeSiMe}_2)_2\text{O}]_2$ [17].

The structural study underscores the fact that a N atom is favoured over a Cl atom in the bridge even when an SiN linkage is present. Table 9 shows the dependence of the Si–N(cn4) bond length on the nature of the other nitrogen substituents. Presumably the increase in length evident in Table 9 from $[\text{NaN}(\text{SiMe}_3)_2]$ [20] to **C1**, 0.108(5) Å, reflects a decreasing tendency of the electrons formally used in forming the metal–nitrogen bonds to be delocalized into the Si–N bonds. It might also be argued that the bond lengthening follows the lowering of negative charge on the N atom which might plausibly be expected in this series. However, we note that the Al–N(cn3) bond length is rather insensitive to the Al coordination number and thus to the formal charge on the Al atom. A similar insensitivity was noted for Be–N(cn3) lengths [17]. Quaternarization of a tertiary N atom might also increase its single-bond radius, as might be indicated by the



(Me = methyl, ^tBu = t-butyl)



difference in N(cn3)-C and N(cn4)-C bond distances. The observed difference, 0.041(4) Å, is, however, much less than the effects on the Al-N and Si-N valencies.

Recently the five- [21] and four-membered [22] cycloalumasilazanes **G** and **H** were synthesized in Braunschweig by the research groups of Wannagat and Veith respectively, and also shown to be dimeric.

Experimental

Preparation of **C1**: 5.0 g (0.024 mol) **I** were lithiated in 50 ml petroleum ether (50–70°C) with 3.1 g butyllithium (0.048 mol) in n-hexane solution (15%). The resulting suspension was cooled to –60°C and a solution of 3.25 g (0.024 mol) AlCl₃ in 10 ml benzene and 10 ml triethylamine was added dropwise. The mixture was allowed to warm slowly (12 h) to room temperature and then refluxed briefly (0.5 h). A grayish-brown precipitate (LiCl) was filtered off and the solvent was removed under reduced pressure. The granular residue (2.5 g) was crystallized from 50 ml of petroleum ether/benzene (8/1). Large, cubic, colourless crystals of pure **C1** were obtained in a yield of 1.4 g (22%).

The NMR spectra were obtained with Varian EM 390 (¹H in C₆H₆), Bruker WM 250 (¹H in C₆D₆ and in CDCl₃), Varian FT 80 (¹³C and ²⁹Si) and Jeol FX-100 (²⁷Al) spectrometers. The infrared spectrum (Nujol mull) was recorded with a Perkin-Elmer 580 B instrument. The Kr⁺ 6471 Å excited Raman spectrum of crystalline material was obtained with a Cary 82 spectrometer, wave number accuracy ± 3 cm⁻¹. The mass spectrum was recorded with an ATLAS-CH-7 spectrometer.

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